8.2 THE VAN DER WAALS INTERACTION

The Van der Waals interaction is the long range, $1/R^6$, attraction between all atoms and molecules. It is essentially a dipole-dipole interaction. Although the dipole moment of an isolated atom vanishes, the instantaneous dipole in one atom can induce a moment in a nearby atom, giving rise to a second order interaction. We consider two one-electron atoms whose nuclei are separated by distance R. The co-ordinates of each electron relative to its nucleus are r_a and r_b, respectively. Expressing the interaction energy of the system in a multipole expansion yields a leading term

$$H' = \frac{1}{R_3} (x_a x_b + y_a y_b - 2 z_a z_b)$$

$$= \frac{1}{R^3} (d_a \cdot d_b - 3 \, d_a \cdot \hat{R} \, d_b \cdot \hat{R}). \tag{8.2-1}$$

If $|g>$ is the ground state of the system, then $<g|H'|g> = 0$. The second order interaction is

$$W_g = - \sum_n \frac{<g|H'|n><n|H'|g>}{E_n - E_g} , \tag{8.2-2}$$

where, as usual, n ranges over all states of the system except g. The interaction is reminiscent of the polarization energy of a single atom, and various expression are available in terms of oscillator strengths. An approximate expression that illustrates the

physically important parameters is

$$W = -\frac{3}{2}\,\bar{E}\,\frac{\alpha_a\,\alpha_b}{R^6}\,, \tag{8.2-3}$$

where α_a and α_b are the polarizabilities of the two atoms, and $\bar{E}$ is a mean excitation energy given by

$$\frac{1}{\bar{E}} = \frac{1}{E_{Ia}} + \frac{1}{E_{Ib}}\,. \tag{8.2-4}$$

Here, E_{Ia} and E_{Ib} are the ionization energies of the two atoms.

The Van der Waals interaction includes higher order terms, of the form B/R^8, C/R^{10}, etc. However, our concern here is not with the specifics of the interaction but how it relates to the ideas of coherence between atoms. For this purpose, we will invoke a model that is centered on the essentials of the interaction.

We consider two identical L-C circuits which are close enough to be electrostatically coupled by the fringing fields of their capacitors. Essentially, the charged capacitors behave like electric dipoles with magnitude $\mu = dQ$, where d is the separation of the plates. The equations of motion for the two circuits are
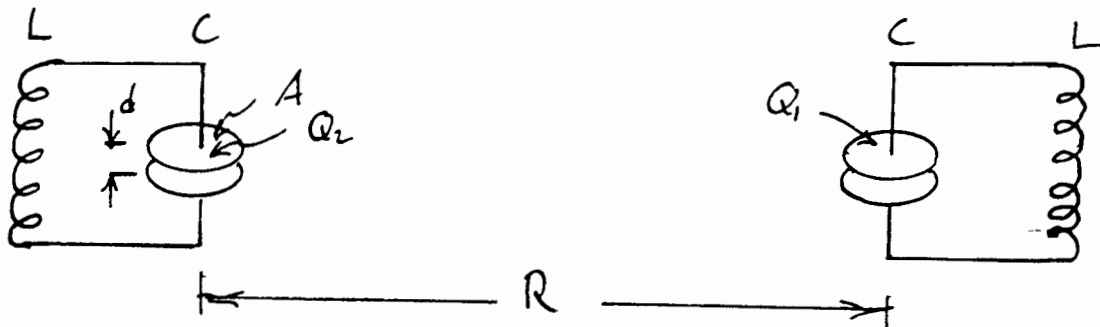
$$L\ddot{Q}_1 + \frac{Q_1}{C} = \frac{Q_2\,d^2}{R^3}\,; \qquad L\ddot{Q}_2 + \frac{Q_2}{C} = \frac{Q_1\,d^2}{R^3}\,. \tag{8.2-5}$$

The capacitance is $A/4\pi d$ (esu units) where A is the area of the capacitor plate. Introducing $\omega_0 = 1/\sqrt{LC}$ and the coupling constant $\kappa = A\,d/(4\pi R^3)$, we have

$$\ddot{Q}_1 + \omega_0^2 Q_1 = \kappa\,\omega_0^2\,Q_2 \tag{8.2-6}$$

with an identical equation for circuit 2. The normal mode frequencies are given by

$$\omega = \omega_0\,\sqrt{1 \pm \kappa}\,. \tag{8.2-7}$$

Now let us quantize the oscillators. We shall assume that they are initially uncoupled ($R \to \infty$), so that the energy is

$$W_0 = W_{1,0} + W_{2,0} = (n_1 + \tfrac{1}{2}) \hbar \omega_0 + (n_2 + \tfrac{1}{2}) \hbar \omega_0 . \tag{8.2-8}$$

For the interacting systems, the energy is

$$W' = W_{1,0} + W_{2,0} = (n_+ + \tfrac{1}{2}) \hbar \omega_+ + (n_- + \tfrac{1}{2}) \hbar \omega_- , \tag{8.2-9}$$

where ω_+ and ω_- are $\omega_0 \sqrt{1+\kappa}$ and $\omega_0 \sqrt{1-\kappa}$, respectively.

Consider the case where the system is in the ground state ($n_1 = n_2 = n_+ = n_- = 0$). If the systems are brought together from a large distance, the interaction energy is

$$W = W' - W_0 = \frac{1}{2} \hbar (\omega_+ + \omega_- - 2\omega_0) . \tag{8.2-10}$$

Expanding $\sqrt{1 \pm \kappa}$ to second order, we obtain

$$W = -\frac{1}{8} \hbar \omega_0 \kappa^2 = -\frac{1}{8} \hbar \omega_0 \left(\frac{A \, d}{4\pi} \right)^2 \frac{1}{R^6} . \tag{8.2-10}$$

We can put this in an even more familiar form by noting that if the capacitor plates are placed in a field E, parallel to their axis, the induced charge is $EA/4\pi$, so that the induced dipole moment is $EAd/4\pi$. Hence, the capacitor's polarizability is $\alpha = A \, d / 4\pi$, and

$$W = -\frac{1}{8} \hbar \omega_0 \frac{\alpha^2}{R^6} . \tag{8.2-11}$$

Comparing this with Eq. 8.2-3, we see that we can regard the Van der Waals interaction as arising from an alteration of the mode structure of the system and the consequent change in the zero-point energy. Although the Van der Waals interaction was originally deduced by a classical argument, the factor $\hbar \omega_0$ reveals that it is fundamentally quantum mechanical. The classical argument implicitly invokes a ground state energy in the system, but classically a charged system will always collapse. The existence of a ground state is quantum mechanical.

8.3 THE FIRST ORDER VAN DER WAALS INTERACTION AND SUPERRADIANCE

Continuing with our model of two interacting oscillators, suppose we consider the system with one quantum of excitation. However, we must be careful about assigning the excitation to one of the modes of the system. For example, if we assign it to one of the uncoupled oscillators, say oscillator a, then as the system is brought together and the modes split, the excitation will be in a superposition of the + and - modes. So, let us

assume we excite one of the modes, say the + modes, with the oscillators separated by some distance R, and then let $R \rightarrow \infty$. The interaction energy is the opposite of this energy shift. Expanding the frequency to first order in κ, we have

$$W = \hbar (\omega_+ - \omega_0) \cong \frac{\kappa}{2} \hbar \omega_0 = \hbar \omega_0 \frac{\alpha}{2 R^3} \ . \qquad (8.3\text{-}1)$$

This is a first-order dipole interaction, arising from the coherence between the two oscillators. Note that if the ω_- mode were excited, the interaction would be attractive. Actually, the sign of the interaction depends not only on the mode, but on the orientation. From Eq. 8.2-1, it is can be seen that if the dipole axes were parallel to **R**, rather than perpendicular, the signs of the interactions would be reversed. Consequently, the symmetric and antisymmetric states both have attractive and repulsive configurations.

The Van der Waals force is often known as the dispersion force, and the first order interaction we have just calculated is called the resonant dispersion interaction. However, it is most naturally described in terms of superradiance. The two quantized oscillators constitute a two-particle superradiant system. If they are excited in phase, the system is superradiant. If they are out of phase they have no net dipole moment, and the system is subradiant. Accompanying superradiance is an interaction energy that is large on the scale of normal interactions. The R^{-3} resonant interaction is both large and extremely long range. It can bind atoms at distances which are huge compared to normal molecular diameters. Molecules bound by the R^{-3} interaction are known as long-range molecules. Such molecules have been known for many years, but it is only recently that they have been made under conditions in which they can be studied clearly. To form such a molecule, two atoms must absorb a photon when they are close, the characteristic length being $\lambda/2\pi$. Such a transition is called a free-to-bound transition. The rate increases as the temperature is decreased, and the molecules are formed with trapped atoms at microkelvin temperatures. The molecular spectrum is characterized by regularly spaced vibrational levels whose spacing can be computed directly from the coefficient of the R^{-3} interaction. However, they also carry another signature: the lifetime of the two-atom superradiant system is 1/2 the lifetime of an isolated atom.

A recent reference on long range molecules is J.D. Miller et al, Phys. Rev. Lett. **71**, 2204 (93).

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